

Thermophysical Property Measurement on Chemically Reacting Systems—a Case Study

Volume 91

Number 3

May–June 1986

Thomas J. Bruno and Gerald C. Straty

National Bureau of Standards
Boulder, CO 80303

This short paper describes several experimental approaches for dealing with chemical reactions or decomposition which can occur when making thermophysical property measurements at high temperature and high pressure. The associated equipment was designed and built to allow thermophysical property data to be cast in a more realistic perspective by taking explicit account of

chemical changes which may occur during an experiment. As an example of these methods, the measurements on the methanol system are discussed in detail.

Key words: chemically reacting systems; decomposition; high temperature; methanol; thermophysical properties.

Accepted: November 18, 1985

1. Introduction

Recent work on the PVT (pressure-volume-temperature) [1]¹ and VLE (vapor-liquid equilibrium) properties [2] of methanol at high temperature and high pressure has demonstrated the need to take explicit account of the possibility of chemical reactions occurring during thermophysical property measurements [3]. The major factors which govern these reactions are the result of thermodynamic, kinetic, and catalytic effects. Thermodynamic factors include activation energies and equilibrium positions. The primary kinetic consideration is the strong temperature and density (concentration) dependence of the rate constant. The experimental apparatus itself may contribute significantly to

chemical reactions by serving as a catalytic agent. While it is clear that the measurement apparatus may be the major factor in fluid decomposition [4], it is equally clear that it will not be possible to build a separate instrument for each fluid. We have therefore designed and applied several sampling and pilot simulation systems to conventional analytical instrumentation in order to assess the extent of chemical react or decomposition which might be expected in a measurement system. In this short paper, we will describe some of these techniques and discuss the measurements on the methanol system as an example of their use.

2. Experimental

The principal experimental apparatus for reaction screening in conjunction with thermophysical property measurement is a laboratory scale batch-semibatch reactor. This reaction screening apparatus is shown schematically in figure 1, and is described fully elsewhere [5]. The heart of the apparatus is a small, thick walled pressure vessel

About the Authors: Thomas J. Bruno and Gerald C. Straty are with the Thermophysics Division, part of NBS' National Engineering Laboratory. The work they describe was supported by the Department of Energy, Office of Basic Energy Sciences.

¹ Figures in brackets indicate literature references.

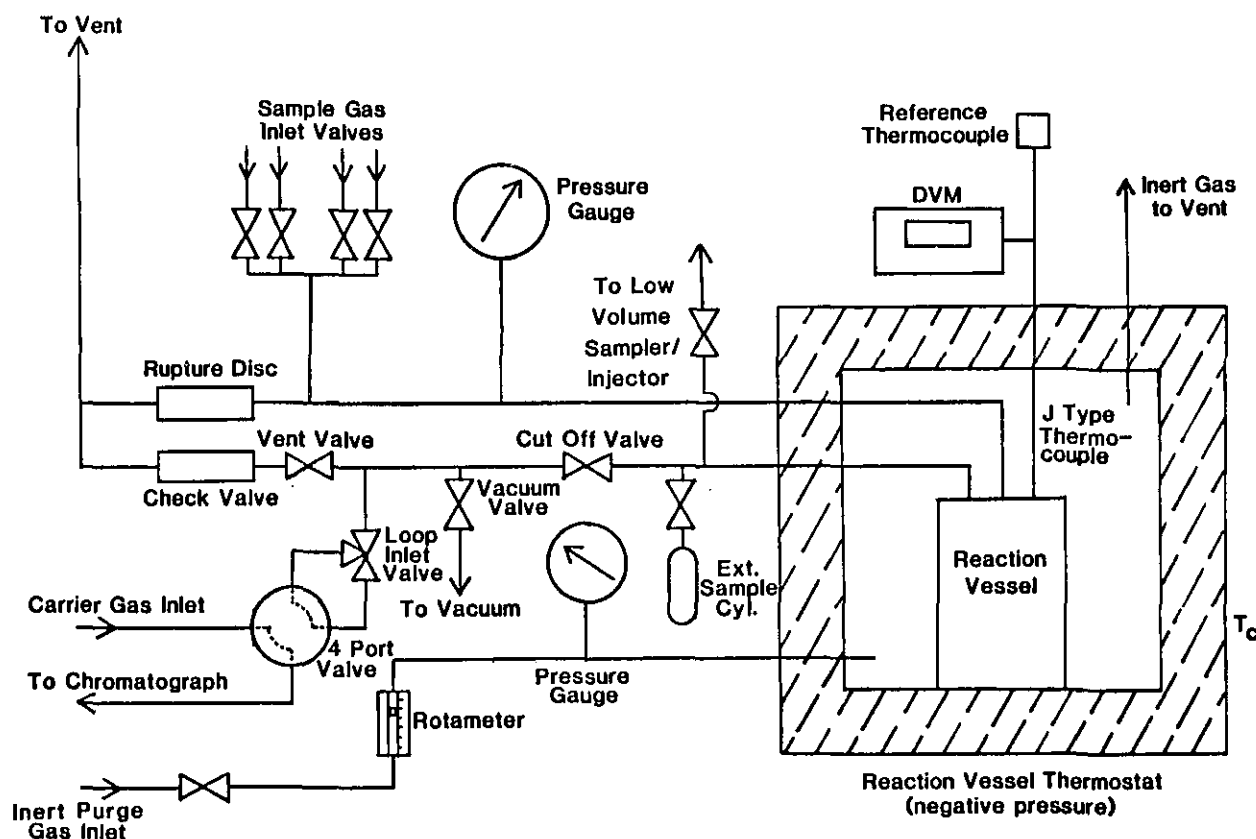


Figure 1—Laboratory scale batch-semibatch reactor.

(316L stainless steel). The vessel incorporates a bolted closure which is sealed using either a 25% glass filled PTFE gasket (for temperatures up to 240 °C) or a 316L stainless steel gasket (for temperatures as high as 450 °C). At 250 °C, the vessel can safely contain a pressure of 130 MPa [6]. The vessel is contained within a specially constructed oven which is maintained at a slight negative pressure gradient (using an air or water transvector) during operation.

Sampling and analysis of the contents of the pressure vessel can be done in several ways during the course of a screening test. The sample line is connected to a modified chromatographic four-port sampling valve which is in turn connected to an analytical chromatograph. This chromatograph is equipped with an ultrasonic (sound velocity) detector, and is primarily used for gas analysis. Alternatively, sample may be collected in a sampling cylinder (which may be quenched in liquid nitrogen) for off-line analysis. This makes possible the use of mass spectroscopy and spectrophotometry, as well as more specific tests.

An additional option for chromatographic analysis of the vessel contents is the use of a low volume sampler-injector. This apparatus, which is shown

schematically in figure 2, is fully described elsewhere [7]. In practice, this injector is installed in place of the external sampling cylinder which is shown in figure 1. This device allows the manipulation and injection of small volumes of gaseous samples, which is advantageous when hazardous materials may be involved. The precision that is possible with this injector is far better than that obtainable with commercial injectors that depend upon the use of relatively large sample volumes in order to achieve a reasonable degree of precision.

As a rough indication of the catalytic effect (and nominal temperature dependence) of wetted surfaces inside a measurement apparatus, reaction chromatography is often useful. In this technique, a bed of granular or powdered material precedes the separation column. This bed is composed of the material that makes up the construction of the measurement apparatus and is maintained at the same temperature as the separation column. It is then possible in a gross manner to determine the onset temperature of chemical decomposition or polymerization. One can then identify reaction products using mass selective detection (mass spectroscopy) or by comparison of the retention times of injected standards. There are a number of drawbacks to this technique, and it therefore must

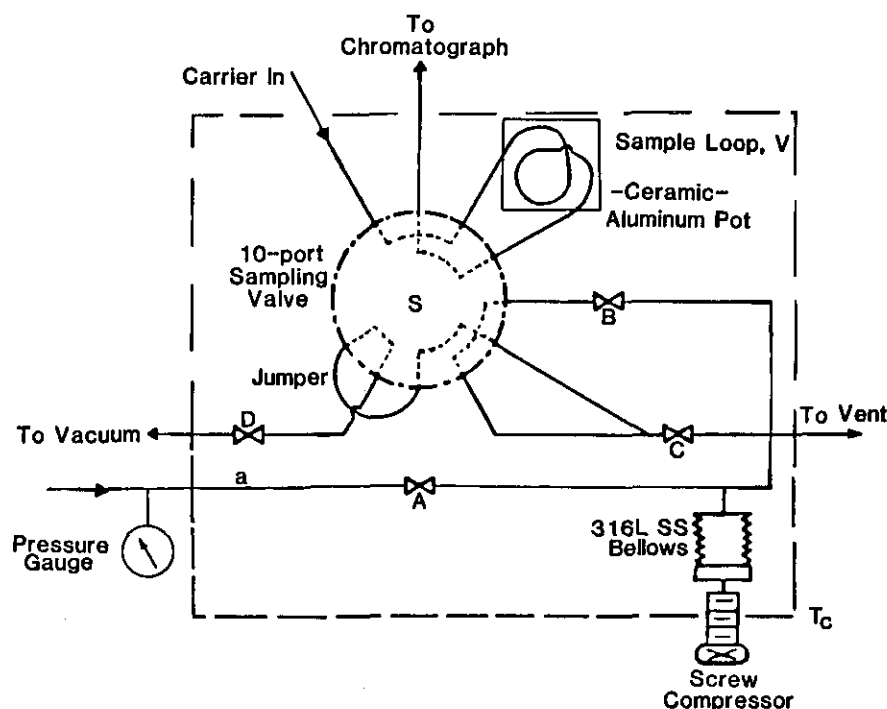


Figure 2—Low volume sampler-injector

be used with great care. The chromatographic column is normally operated at low pressure, and the sample is diluted by the carrier gas. In addition, the ratio of the sample mass to surface area (of the bed material) is essentially uncontrollable. It is therefore unreasonable to expect exact duplication of the conditions in a PVT or VLE apparatus. From a chromatographic point of view, the use of the bed with capillary columns is inconvenient. This problem is of little consequence when the analyte is gaseous or volatile, since packed columns (especially porous polymer packings) will perform very well. As the temperature of the bed and separation column is increased during the course of a screening test, the carrier gas flow rate will need to be reduced. This change in flow will limit quantitative accuracy to no better than 2 percent, regardless of the method of detection and calibration employed.

In addition to the methodology applied to gas chromatography, liquid chromatography and infrared and ultraviolet spectrophotometry have found some use in reaction screening for thermophysical property measurements. The inherently lower efficiency of liquid chromatography and the need to make the transition from the high temperature region to essentially ambient temperature have limited its usefulness in this application. Infrared spectrophotometry (IR) can often provide valuable information, especially on simple, one component

systems such as methanol or benzene [1,8]. The spectra are measured on samples collected from the reactor (fig. 1) or directly from the PVT or VLE apparatus. It is often the case that IR will provide useful negative information; knowledge of functional groups that are absent is almost as helpful as knowledge of what is present. Ultraviolet spectrophotometry is employed in the same way as IR, except that the functional group information is far more limited than that provided by IR.

3. Results—Methanol

As mentioned earlier, PVT and VLE studies on pure methanol indicated substantial chemical reaction occurring at temperatures near and above 200 °C. The liquid phase withdrawn (at ambient temperature and pressure) from a high temperature VLE cell [2] was found to be in equilibrium with a significantly large vapor phase fraction. The liquid itself had a strongly rancid odor. The same odor was noted upon withdrawal of methanol from the high temperature PVT apparatus [1] after the methanol was exposed to temperatures in excess of 200 °C. In addition, a measurable residual pressure (due to a gaseous phase) was noted upon condensation of the liquid methanol from the PVT cell using a liquid nitrogen cold trap. This indicated the probable presence of hydrogen and/or carbon

monoxide in the residual gas.

A number of studies involving the techniques described earlier were initiated in order to cast the PVT and VLE measurements in a more useful perspective. An aliquot of methanol was maintained at 250 °C and 3.7 mPa for 48 hours using the apparatus shown in figure 1. Analysis of the gaseous phase (by gas chromatography) after cooling indicated the presence of both hydrogen and carbon monoxide. The liquid phase was found to have the same rancid odor noted previously. Infrared spectrophotometry indicated the presence of an ether linkage in an impurity species present in the liquid. This was confirmed by mass spectrometry, which indicated the presence of dimethylether. Gas chromatographic analysis of the liquid indicated the presence of formaldehyde, and several heavier impurities which could not be identified by their mass spectra alone. Testing the liquid with acidified 2,4-dinitrophenylhydrazine confirmed the presence of formaldehyde by the identification of the red precipitate of the 2,4-dinitrophenylhydrazone. The acidic mother liquor developed further precipitate upon standing, indicating the presence of acetals and hemiacetals [10], which probably make up the heavier impurities found on the chromatogram.

In order to ascertain the catalytic behavior of the 316L stainless steel PVT cell, and to estimate the nominal temperature dependence of the reaction rate and product distribution at elevated temperatures, the reaction chromatography technique described earlier was used. In this approach, a 1.5 m long, 0.6 cm o.d. stainless steel column was almost completely filled with Chromosorb 102², with the final 5 cm at the column inlet being made up with powdered 316L stainless steel. Injected samples of pure methanol then pass over the bed of powdered stainless steel before the resulting sample plug is applied to the separation column. Example results from this study are given in table 1, along with data taken on a column differing only in the absence of the powdered stainless steel bed. The area percent measurements were made using helium carrier gas and thermal conductivity detection. The flow rate was decreased as the temperature was increased; thus the reported percent compositions of light (more volatile than methanol) and heavy (less volatile than methanol) reaction products are only approximate. Serious decomposition/reaction

Table 1

Temperature °C	Area Percent Methanol	Area Percent Light Impurities	Area Percent Heavy Impurities
REACTION COLUMN			
100	99.8	0.2	0
200	95.2	1.0	3.8
250	85.7	0.3	14.0
CONTROL COLUMN			
100	100	0	0
200	100	0	0
250	100	0	0

problems are seen to begin at 200 °C, and become extremely severe at 250 °C. Hydrogen was produced at a temperature between 210 and 225 °C. Carbon monoxide, another highly probable product at this temperature, could not be resolved from the methanol peak.

The results discussed above are in general agreement with earlier observations [4]. Analyses done on each methanol charge in the PVT experiment yielded results which were expected on the basis of these reaction screening studies. Corrections were made to the PVT data of methanol on the basis of these studies of the onset of reactions, and are fully described elsewhere [1].

4. References

- [1] Straty, G. C.; A. M. F. Palavra and T. J. Bruno, PVT properties of methanol at temperatures to 300 °C, *Int. J. Thermophys.* (in press).
- [2] Mayrath, J. E. (in preparation).
- [3] Hanley, H. J. M., Position statement on chemically reacting systems (a copy of which may be obtained via personal communication with the author of this paper) (1984).
- [4] Ta'ani, R. Doctoral Dissertation, Karlsruhe University (1976).
- [5] Bruno, T. J., and G. L. Hume, A high temperature, high pressure reaction screening apparatus, *J. Res. Natl. Bur. Stand. (U.S.)*, **90** (3), 255 (1985).
- [6] ASME Boiler and Pressure Vessel Code, Sec. VIII: Unfired Pressure Vessels. New York: American Society of Mechanical Engineers (1965).
- [7] Bruno, T. J., A simple gas sampling and injection apparatus. *J. Chromatogr. Sci.* **23**, 325 (1985).
- [8] Straty, G. C.; M. J. Ball and T. J. Bruno, PVT properties of benzene at temperatures to 450 °C, *Int. J. Thermophys.* (in preparation).
- [9] Straty, G. C., and A. M. F. Palavra, Automated high-temperature PVT apparatus with data for propane, *J. Res. Natl. Bur. Stand. (U.S.)* **89** (5), 375 (1984).
- [10] Svoronos, P. D. N., City University of New York, Bayside, NY, 11364, private communication (1984).

² Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.